

FORM PTO-1390 (REV. 9-2001)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER 31223-81764 (F-755)
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371			U.S. APPLICATION NO. (If known, see 37 CFR 1.5) 10/009625
INTERNATIONAL APPLICATION NO. PCT/EP00/05397	INTERNATIONAL FILING DATE June 8, 2000	PRIORITY DATE CLAIMED June 10, 1999	
TITLE OF INVENTION Polypropylene with High Melt Strength and Drawability			
APPLICANT(S) FOR DO/EO/US DUPIRE, Marc; MICHEL, Jacques			
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:			
<p>1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.</p> <p>2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.</p> <p>3. <input type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.</p> <p>4. <input type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31).</p> <p>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2))</p> <p>a. <input checked="" type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau).</p> <p>b. <input type="checkbox"/> has been communicated by the International Bureau.</p> <p>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</p> <p>6. <input type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).</p> <p>a. <input type="checkbox"/> is attached hereto.</p> <p>b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4).</p> <p>7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))</p> <p>a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau).</p> <p>b. <input type="checkbox"/> have been communicated by the International Bureau.</p> <p>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</p> <p>d. <input type="checkbox"/> have not been made and will not be made.</p> <p>8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).</p> <p>9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).</p> <p>10. <input type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</p> <p>Items 11 to 20 below concern document(s) or information included:</p> <p>11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</p> <p>12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</p> <p>13. <input checked="" type="checkbox"/> A FIRST preliminary amendment.</p> <p>14. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment.</p> <p>15. <input type="checkbox"/> A substitute specification.</p> <p>16. <input type="checkbox"/> A change of power of attorney and/or address letter.</p> <p>17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.</p> <p>18. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4).</p> <p>19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).</p> <p>20. <input checked="" type="checkbox"/> Other items or information: Copy of PCT Request Copy of International Search Report</p>			

U.S. APPLICATION NO. (if known) (37 CFR 1.5)

10/009625

INTERNATIONAL APPLICATION NO.
PCT/EP00/05397

ATTORNEY'S DOCKET NUMBER
31223-81764

21. ☐ The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):

Neither international preliminary examination fee (37 CFR 1.482)
nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO
and International Search Report not prepared by the EPO or JPO \$1040.00

International preliminary examination fee (37 CFR 1.482) not paid to
USPTO but International Search Report prepared by the EPO or JPO \$890.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO
but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$740.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO
but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$710.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO
and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00

ENTER APPROPRIATE BASIC FEE AMOUNT =

CALCULATIONS PTO USE ONLY

\$ 890.00

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☒ 30
months from the earliest claimed priority date (37 CFR 1.492(e)).

\$ 130.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$
Total claims	- 20 =		x \$18.00	\$
Independent claims	- 3 =		x \$84.00	\$
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$280.00	\$

TOTAL OF ABOVE CALCULATIONS = \$ 1,020.00

☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above
are reduced by 1/2.

+

SUBTOTAL = \$ 1,020.00

Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(f)).

\$

TOTAL NATIONAL FEE = \$ 1,020.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +

\$

TOTAL FEES ENCLOSED = \$ 1,020.00

Amount to be
refunded: \$

charged: \$

- a. ☒ A check in the amount of \$ 1,020.00 to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees.
A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
overpayment to Deposit Account No. 12-1781. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. Credit card
information should not be included on this form. Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR
1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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ATTENTION: Lenora Evans
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SIGNATURE

William D. Jackson

NAME

20,846

REGISTRATION NUMBER

31223-81764
(F-755)

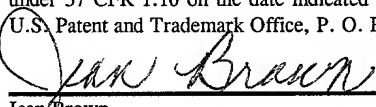
TRANSMITTAL LETTER
TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US)
FOR ENTRY INTO THE U.S. NATIONAL PHASE (Chapter 2)

INTERNATIONAL APPLICATION NO. PCT/EP00/05397	INTERNATIONAL FILING DATE June 8, 2000	PRIORITY DATE CLAIMED June 10, 1999
TITLE OF THE INVENTION POLYPROPYLENE WITH HIGH MELT STRENGTH AND DRAWABILITY		
APPLICANT(S) FOR DO/EO/US DUPIRE, Marc; MICHEL, Jacques		
PRIORITY APPLICATION NO. EP 99 111 318.4		

Via Express Mail

Box PCT
U.S. Patent and Trademark Office
P. O. Box 2327
Arlington, VA 22202

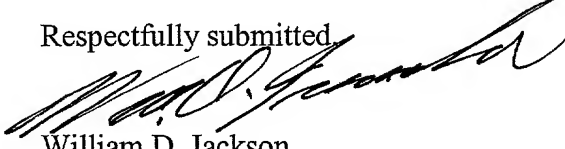
Dear Sir:

EXPRESS MAIL CERTIFICATE OF MAILING	
Express Mail Mailing Label No. EL 465 446 331 US	
I hereby certify that the papers enclosed herein are being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated below and addressed to: Box PCT, U.S. Patent and Trademark Office, P. O. Box 2327, Arlington, VA 22202:	
 Jean Brown	December 10, 2001 Date of Deposit

Submitted herewith under cover of Form PTO-1390 is a copy of the International Application as filed (35 U.S.C. § 371(c)(2) along with a Preliminary Amendment. An English language translation of the application is not required since the International Application is being filed in English.

Also submitted herewith is a check in the amount of \$1,020.00 as the fee for entry into the national phase as calculated on the attached Form PTC-1390. An oath or declaration of the inventor under 35 U.S.C. § 371(c)(4) will be submitted later.

Respectfully submitted


William D. Jackson
Registration No. 20,846

Date: December 10, 2001

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JC07 Rec'd PCT/PTO 10 DEC 2001

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31223-81764
(F-755)

**TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US)
FOR ENTRY INTO THE U.S. NATIONAL PHASE (Chapter 2)**

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP00/05397	June 8, 2000	June 10, 1999
TITLE OF THE INVENTION		
POLYPROPYLENE WITH HIGH MELT STRENGTH AND DRAWABILITY		
APPLICANT(S) FOR DO/EO/US		
DUPIRE, Marc; MICHEL, Jacques		
PRIORITY APPLICATION NO.		
EP 99 111 318.4		

Box PCT
U.S. Patent and Trademark Office
P. O. Box 2327
Arlington, VA 22202

Sir:

PRELIMINARY AMENDMENT

In the Claims

Cancel claims 1-33.

Add the following new claims 34-53:

34. A method of melt processing a polypropylene blend, the method comprising providing a multimodal polypropylene blend in a molten state, said blend having a melt dispersion index of from 8 to 70 and a ratio M_z/M_n of at least 10 thereby enhancing a

compromise between melt strength and drawability, and processing the blend in the melt by drawing and cooling the blend to form a solid product.

35. A method according to claim 34 wherein the dispersion index is greater than 15.
36. A method according to claim 34 wherein the ratio of M_z/M_n is from 50-150.
37. A method according to claim 36 wherein the dispersion index is greater than 15.
38. A method according to claim 34 wherein the blend is bimodal and comprises from 50 to 70 wt.% of a first high molecular weight fraction and from 50 to 30 wt.% of a second low molecular weight fraction.
39. A method according to claim 38 wherein the ratio of the melt flow indexes of the first and second fraction is at least 5.
40. A method according to claim 34 wherein the blend comprises from 55 to 60 wt.% of the first fraction and from 45 to 35 wt.% of the second fraction.
41. A method according to claim 34 wherein the blend has been formed by reactive extrusion of a mixture of at least two fractions together with a mixture of a chain scission agent and a chain grafting agent.
42. A method according to claim 41 wherein the chain scission agent comprises 2,5-dimethyl-2,5-di(tert-butylperoxy) hexane.
43. A method according to claim 41 wherein the chain grafting agent is selected from the group consisting of allyl methacrylate and divinyl benzene.

44. A method according to claim 34 wherein the polypropylene has a bimodal molecular weight distribution.

45. A method according to claim 34 wherein said solid particle is selected from the group consisting of spun fibers, blown films, foams, thermoformed articles, and extrusions.

46. A multimodal polypropylene blend useful in melt processing and providing for enhancing a compromise between melt strength and drawability, said blend having a dispersion index of at least 8 and a ratio M_z/M_n of at least 10.

47. A multimodal polypropylene blend according to claim 46 wherein the dispersion index is greater than 15.

48. A multimodal polypropylene blend according to claim 46 wherein the ratio M_z/M_n is from 50-150.

49. A multimodal polypropylene blend according to claim 48 wherein the dispersion index is greater than 15.

50. A multimodal polypropylene blend according to claim 46 wherein the blend is bimodal and comprises from 50 to 70 wt.% of a first high molecular weight fraction and from 50 to 30 wt.% of a second low molecular weight fraction.

51. A multimodal polypropylene blend according to claim 50 wherein the ratio of the melt flow indexes of the first and second fractions is at least 5.

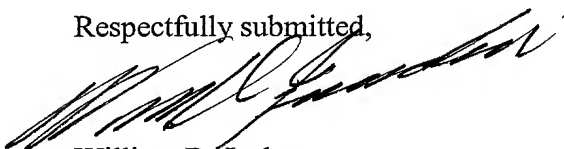
52. A multimodal polypropylene blend according to claim 50 wherein the blend comprises from 55 to 65 wt.% of the first fraction and from 45 to 35 wt.% of the second fraction.

53. A multimodal polypropylene blend according to claim 52 wherein the ratio of the melt flow indexes of the first and second fractions is at least 5.

Remarks

It is respectfully requested that this Preliminary Amendment be entered prior to calculation of the fees.

Respectfully submitted,



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POLYPROPYLENE WITH HIGH MELT STRENGTH
AND DRAWABILITY

The present invention relates to polypropylene.

Isotactic and syndiotactic polypropylene, and blends thereof, are known for use in a number of different applications. For example, polypropylene is used for the manufacture of spun fibres, blown films, extruded profiles and foams. In such applications in which the polypropylene is processed while molten, it is desirable for the polymer to have a high melt strength. For some applications, for example fibre spinning and film blowing, as well as having a high melt strength the polypropylene is required to have a high drawability. A high drawability not only enables the fibres or films to be produced at high speed without fracture, but also enables finer diameter fibres and thinner films to be manufactured.

There tends to be a compromise between high melt strength and drawability. Thus some known polypropylenes have high melt strength but low drawability. This makes them unsuitable for drawing fibres, particularly of small diameter.

A polymer melt having high melt strength at high shear rates refers to a melt that becomes stiffer and stronger when stretched, rather than one that thins out and breaks when stretched. This stiffening upon drawing is commonly called strain-hardening. Polypropylene processing operations where melt strength plays an important role include blow moulding, extrusion coating, thermoforming, fibre spinning and foam extrusion. In thermoforming, a poor melt strength results in a sagging phenomenon. In fibre spinning, a poor melt strength can result in undesired movements of the fibres due to transverse forces, for example by cooling air, which ultimately can lead to

"married" fibres and fibre breakage. On the other hand, a too-high melt strength will limit the achievement of low titre fibres. Accordingly, a correct balance between melt strength and drawability is desirable. For blown (biaxially oriented) or cast films also, a correct balance between melt strength and stretchability is very important. In foam extrusion, a poor melt strength results in cell rupture and non-uniform cell structure. For such an application, a poor drawability will limit the fineness of the walls.

Several solutions have been proposed in the prior art to increase the melt strength of polypropylene. For example, polymers with long chain branching tend to exhibit good melt strength. For isotactic polypropylene, this can be achieved by irradiation or by reactive extrusion processes, such as disclosed in US-A-5047446, 5047485 and 5541236. The limitation of these processes is the significant reduction of drawability occurring at the same time as melt strength increases. In addition, the irradiation process is expensive. It has also been proposed to blend isotactic polypropylene with additives, such as high molecular weight acrylates, to increase the melt strength, as disclosed for example in EP-A-0739938. The same results can be achieved by blending with isotactic polypropylene polyethylene having high melt strength or fillers. These processes are limited by the strong modification by the additives of the intrinsic properties of the isotactic polypropylene.

It is also known from the literature that the melt strength of isotactic polypropylene is solely determined by its weight average molecular weight (Mw) (A.Gijsels Ind. Polym. Process., 9, 252 (1994)).

US-A-5549867 relates to a melt spinning process for polyolefin resins in which a blended resin includes a relatively small portion of a low molecular weight high melt flow rate narrow molecular weight distribution polyolefin resin with a larger

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portion of a miscible high molecular weight, low melt flow rate and typically narrow molecular weight distribution polyolefin resin. It is disclosed that the enhanced molecular weight distribution polyolefin blended resin has a variety of property parameters, including a molecular weight distribution breadth M_z/M_n of between 7.2 and 10, a flow rate ratio of less than 15.5 and a power law index at 20 seconds⁻¹ of between 0.70 and 0.78 and either a Z-average molecular weight M_z of between 400,000 and 580,000, or a second order constant b_2 determined from the regression analysis viscosity equation of between -0.029 and -0.047 or both, and unless both of the M_z and b_2 parameters is within said ranges, a die swell B^2 of between 1.6 and 2.0 and a spinnability factor $\ln(B^2)/MFR$ of between about 0.08 and about 0.026.

US-A-5494965 discloses a process for manufacturing bimodal olefin polymers and copolymers. However, the specification does not address the problems of drawing polypropylenes.

US-A-5578682 discloses the bimodalisation of a polymer molecular weight distribution by using grafting and scission agents.

EP-A-0310734 discloses catalyst systems for producing polyolefins having a broad molecular weight distribution, in particular a multimodal molecular weight distribution. This specification does not address the problems of drawability of polypropylenes.

It is an aim of the present invention to provide polypropylene, which may be isotactic, syndiotactic or a blend of isotactic and syndiotactic fractions, which provides improved properties such as melt strength and drawability. It is also an aim of the present invention to provide such polypropylene which can be used in processing applications which require the polypropylene to be processed from the melt, for example at high shear rates, typically in fibre spinning. It is a further aim of the present invention to provide polypropylene which has an improved

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compromise between melt strength and drawability.

Accordingly the present invention provides the use of a multimodal isotactic polypropylene blend in melt processing wherein for enhancing a compromise between melt strength and drawability the blend has a dispersion index of at least 8 and a ratio M_z/M_n of at least 10.

The present invention also provides a method of enhancing a compromise between melt strength and drawability in melt processing of a polypropylene, the process including providing a multimodal polypropylene blend having a dispersion index of at least 8 and a ratio M_z/M_n of at least 10.

The present invention further provides a method of melt processing a polypropylene blend, the method comprising providing a multimodal polypropylene blend, selecting the blend to have a dispersion index of from 8 to 70 and a ratio M_z/M_n of at least 10 thereby enhancing a compromise between melt strength and drawability, and processing the blend in the melt by drawing the blend to form a solid product.

In this specification, the dispersion index (D) (also known as the polydispersity index) is the ratio between the weight average molecular weight (M_w) and the number average molecular weight (M_n). The ratio M_z/M_n is the molecular weight distribution breadth. M_z is the z-average molecular weight, defined as $\sum N_i M_i^3 / \sum N_i M_i^2$ over all i .

The multimodal blend is preferably bimodal, but may alternatively be trimodal, tetramodal, etc.. The blend of the fractions may be obtained by physical blending or chemical blending, for example chemical blending using two reactors in series or chemical blending using one reactor with specific dual-type catalysts. The polypropylene fractions may be composed of

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homopolymer or copolymer and may be made using differing catalysts, for example Ziegler-Natta catalysts or metallocene catalysts.

Preferably, the dispersion index is greater than 15. The dispersion index may be up to about 70.

The molecular weight distribution breadth is not especially limited, provided that it is 10 or above. Preferably, the molecular weight distribution breadth (M_z/M_n) is from 50-150.

The blend may comprise from 20 to 80 wt% of a first high molecular weight fraction and from 80 to 20 wt% of a second low molecular weight fraction.

Preferably, the blend comprises from 50 to 70 wt% of the first fraction and from 50 to 30 wt% of the second fraction.

More preferably, the blend comprises from 55 to 65 wt% of the first fraction and from 45 to 35 wt% of the second fraction.

Preferably, the ratio of the melt flow indexes of the first and second fractions is at least 5. Typically, the first fraction has a melt flow index of less than 5 dg/min and the second fraction has a melt flow index of from 60 to 1000 dg/min.

Optionally, the blend has been formed by reactive extrusion of a mixture of the first and second fractions together with a mixture of a chain scission agent and a chain grafting agent.

The chain scission agent may comprise 2,5-dimethyl-2,5-di(tert-butylperoxy) hexane. The chain grafting agent may be selected from allyl methacrylate and divinyl benzene.

The first and second fractions, and the blend, are preferably comprised of polypropylene homopolymer. Alternatively, the first and/or second fractions may be comprised of polypropylene

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The present invention also relates to the use of the polypropylene for forming fibres, foams, films, thermoformed articles and extruded products.

The melt strength tends to increase with a decrease in the melt flow index (MFI) of the polypropylene. In this specification, the MFI values are determined using the procedures of ASTM D1238 using a load of 2.16kg at a temperature of 230°C.

As well as having high melt strength, it is desired for fibre spinning (and film blowing) that the polypropylene has a high drawability. A high drawability represents the ability of the material to be stretched into a small diameter fibre (or a thin film) at high speed, i.e. at high strain rates. Typically, the drawability of the polypropylene is determined by wrapping a fibre around a wheel rotating at constant acceleration during

spinning of the fibre and measuring the maximum angular speed, in units of revolutions per minute, up to rupture of the filament. With increasing drawability, the speed of drawing can increase prior to rupture, thereby enabling even finer filaments to be manufactured.

Thus the present inventors have found that by providing a polypropylene blend with a dispersion index of at least 8, the melt strength and drawability together can be sufficiently high to yield a good compromise between them, enabling the blend to have particularly advantageous application for fibre spinning.

The present invention will now be described by way of example only, with reference to the accompanying drawings, in which: Figures 1 to 3 are gel permeation chromatograms (GPCs) of isotactic polypropylene resins in accordance with three different embodiments of the invention.

Referring to Figure 1, there is shown a GPC chromatogram of a bimodal isotactic polypropylene in accordance with a first embodiment of the present invention. The bimodal isotactic polypropylene has a melt flow index of 11.5 dg/min. The molecular weight distribution (A) of the bimodal isotactic polypropylene is such that Mw is 279 kDa, Mn is 30 kDa and the dispersion index is accordingly 9.3. The bimodal isotactic polypropylene is formed as a physical blend of two isotactic polypropylene homopolymer fractions. The first fraction is a high molecular weight fraction (B) having an MFI of 2.3 dg/min and comprising 55 wt% of the bimodal isotactic polypropylene.

The second fraction is a low molecular weight (C) fraction having an MFI of 72 dg/min and comprising 45 wt% of the bimodal isotactic polypropylene. The high molecular weight fraction has an Mw of 419 kDa, an Mn of 49 kDa and a dispersion index of 8.6, and the low molecular weight fraction has an Mw of 146 kDa, an Mn of 21 kDa and a dispersion index of 7.0.

Figure 2 is a GPC chromatogram of a bimodal isotactic polypropylene in accordance with a second embodiment of the present invention. The bimodal isotactic polypropylene has a melt flow index of 6.9 dg/min. The molecular weight distribution (A) of the bimodal isotactic polypropylene is such that Mw is 363 kDa, Mn is 26 kDa and the dispersion index is accordingly 14.1.

The bimodal isotactic polypropylene is formed as a physical blend of two isotactic polypropylene homopolymer fractions, the first being a high molecular weight fraction (B) having an MFI of 0.8 dg/min and comprising 57 wt% of the bimodal isotactic polypropylene, and the second being a low molecular weight fraction having an MFI of 350 dg/min and comprising 43 wt% of the bimodal isotactic polypropylene. The high molecular weight fraction has an Mw of 568 kDa, an Mn of 73 kDa and a dispersion index of 7.8, and the low molecular weight fraction (C) has an Mw of 99 kDa, an Mn of 16 kDa and a dispersion index of 6.2.

Figure 3 is a GPC chromatogram of a bimodal isotactic polypropylene in accordance with a third embodiment of the present invention. The bimodal isotactic polypropylene has a melt flow index of 1.1 dg/min. The molecular weight distribution (A) of the bimodal isotactic polypropylene is such that Mw is 671 kDa, Mn is 27 kDa and the dispersion index is accordingly 24.9.

The bimodal isotactic polypropylene is formed as a physical blend of two isotactic polypropylene homopolymer fractions, the first being a high molecular weight fraction (B) having an MFI of 0.06 dg/min and comprising 55 wt% of the bimodal isotactic polypropylene, and the second being a low molecular weight fraction (C) having an MFI of 450 dg/min and comprising 45 wt% of the bimodal isotactic polypropylene. The high molecular weight fraction has an Mw of 1460 kDa, an Mn of 142 kDa and a dispersion index of 10.2, and the low molecular weight fraction has an Mw of 95 kDa, an Mn of 15 kDa and a dispersion index of 6.3.

It may be seen for Figures 1 to 3 that in accordance with the

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embodiments of the invention, each bimodal isotactic polypropylene blend is composed of two initial isotactic polypropylene fractions. The fractions are selected so as to provide a minimum dispersion index (D) of 8 in the bimodal isotactic polypropylene blend. The dispersion index D may be up to about 70 for blends in accordance with the invention. The fractions are also selected so as to have specific respective melt flow indexes, thereby to provide a melt flow index differential between the two fractions, to provide the required minimum dispersion index in the ultimate blend. In this way, the molecular weight distribution of the blend is broadened, which has been found by the inventors to provide increased melt strength at any given melt flow index for the blend. In addition, as the melt flow index of the blend increases, this also tends to decrease the melt strength.

In the blending operation using reactive extrusion, a mixture of a chain scission agent and a chain grafting agent may be employed.

The chain scission agent may for example comprise a peroxide compound, typically 2,5-dimethyl-2,5-di(tert-butylperoxy) hexane. The use of such a chain scission agent combined with a grafting agent tends to increase the degree of branching of the molecules in the high molecular weight fraction, thereby increasing the molecular weight distribution of the ultimate polypropylene, thereby in turn yet further increasing the melt strength.

The grafting agent may be a bi- or multifunctional grafting agent, typically allyl methacrylate or divinyl benzene. The grafting agent promotes cross-linking of the branches formed by the chain scission agent. This increases the melt strength but tends to reduce the drawability or spinnability of the polypropylene.

Typically, the extrusion temperature is around 220°C. When a

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chain scission agent such as 2,5-dimethyl-2,5-di(tert-butylperoxy) hexane is employed, this is employed in an amount of around 55 ppm based on the weight of the blend. When a grafting agent is employed, such as allyl methacrylate, this is typically employed in an amount of around 750 ppm based on the weight of the blend.

The flexural modulus of the polypropylenes is a complex function depending upon several parameters, not only the dispersion index D but also for example the melt flow index, the xylene solubles and the crystallinity of the polymer. The present inventors have also found that the flexural modulus E of the polypropylenes in accordance with the invention tends to increase with increasing dispersion index at constant melt flow index and xylene solubles.

Preferably, the isotactic polypropylenes of the present invention are produced with Ziegler-Natta catalysts using a phthalate as an external electron donor, see for example EP-A-0045976, EP-A-0045977 and US-A-4,544,171. The phthalate may be replaced by a 1,3 diether compound, see for example US-A- 4,971,937, 4,978,648 and 5,095,153. The isotactic polypropylene can also be produced with metallocene catalysts, see for example EP-A-0416566, EP-A-0399348 and EP-A-0336128. The invention also applies to syndiotactic polypropylene, or to a blend of isotactic and syndiotactic polypropylene obtained by physical mixing or chemical mixing using for example a metallocene catalyst, as disclosed for example in US-A-5,036,034. In addition, the polypropylene may be treated with a nucleating agent, typically lithium benzoate, for nucleation of crystallites in the polypropylene.

The polypropylene may be a homopolymer, a random copolymer containing ethylene and a higher alpha-olefin, or a heterophasic block copolymer of ethylene and a higher alpha-olefin.

The present invention will now be described further with

reference to the following non-limiting Examples.

Examples 1 to 4

For each of Examples 1 to 4, a bimodal isotactic polypropylene blend was produced by blending together a high molecular weight component and a low molecular weight component in a screw extrusion apparatus operated under nitrogen gas at a temperature of around 220°C. Table 1 specifies the composition and properties for both the high molecular weight and low molecular weight components, and the ultimate blend for each of Examples 1 to 4. The molecular weight distributions of the blends and components of Examples 2 and 4 are shown respectively in Figures 2 and 3.

For each of Examples 1 to 4, the melt strength was tested by measuring the force for a fibre which is pulled from a melt. In this specification the melt strength was determined in a laboratory using a CEAST rheometer (Rheoscope 1000) equipped with a capillary die and a rotating wheel as a take up device. With this set up, molten polymer is extruded by application of a pressure resulting from the displacement of a piston. The molten extrudate is uniaxially stretched before crystallisation by wrapping the fibre around the rotating wheel. In this test, the piston displacement rate is fixed, and the speed of the rotation take-up wheel is linearly changed, i.e. with constant acceleration, until the fibre, becoming very thin, breaks. The tensile force is recorded during the test. The melt strength is defined as the maximum tensile force corresponding to the breaking of the fibre. The tests were run under standard conditions as follows: the cylindrical die had a length/diameter ratio of 5mm to 1mm; the diameter of the rotating wheel was 12cm; the extrusion temperature was 250°C; the displacement ratio of the piston was 2mm/min, the extrudate throughput was 2.36mm³/min and the acceleration of the rotating wheel was 10rpm/100s or

0.000628m/s². The drawability is defined as the titre at break under the same conditions. The correspondence between the angular speed of the wheel (V) expressed in rpm and the titre (expressed in denier) is the following: titre at break = 3384.4ρ/V where ρ is the polymer density at 250°C. The results are also specified in Table 1.

It may be seen for each of Examples 1 to 4 that the dispersion index D, which is the ratio Mw/Mn, is greater than 8 and the melt flow index varies from 1.1 to 6.9 dg/min. The melt strength varied from 2.8 mN to 15.5 mN. In combination with the melt strength values, the drawability of the polymers of each of Examples 1 to 4 is high, the filament breaking at least 260 rpm at a temperature of 250°C.

Comparative Example 1

As a comparison, the corresponding properties of a commercially available isotactic polypropylene resin with a high degree of long chain branching were tested. The resin is sold under the trade name Profax PF814 by the company Montell North America Inc. of Wilmington, Delaware, USA. It may be seen that while the resin of Comparative Example 1 had a very high melt strength, being around 3 times that of the maximum melt strength of Examples 1 to 4, particularly for that of Example 4, nevertheless the drawability of the commercial resin was very low, with the filament breaking at a speed of only 9 rpm at 250°C.

Comparative Example 2

As a further comparison, the corresponding properties of a monomodal polypropylene resin were tested and the results are shown in Table 1.

Table 1 shows that the multimodal polypropylene resins in

accordance with the invention have a good compromise between high melt strength and high drawability. This is achieved by for example a blend of high and low molecular weight components having a high dispersion index of at least 8. This makes the resins of the invention particularly suitable for fibre spinning and film blowing. The resins of the invention also have utility in lower shear rate processes, such as the formation of films and in extrusion forming processes. The multimodal polypropylene in accordance with the invention can be stretched more than the high melt strength polypropylene with long chain branching of Comparative Example 1. The propylene of the Examples had a higher drawability than the polypropylene of Comparative Example 2. Thus the present invention provides polypropylene blends having an improved compromise of high melt strength and extensibility in the melt.

TABLE 1

	High Mw component		Low Mw component			Blend					Mz (kDa)	Mw (kDa)	Mn (kDa)	Mz/Mn
	wt %	MFI (dg/min)	D	wt %	MFI (dg/min)	D	MFI (dg/min)	D (Mw/Mn)	Melt strength (mN)	Draw-ability (rpm)				
Example 1	65	0.8	7.8	35	63	6.2	2.9	10.1	4.4	>300		453	2313	51.7
Example 2	57	0.8	7.8	43	350	6.2	6.9	14.1	3.0	>300		363	2255	87.7
Example 3	65	1.6	7.1	35	450	6.3	6.9	10.8	2.8	>300		336	1651	53.3
Example 4	55	0.06	10.2	45	450	6.3	1.1	24.9	15.5	260		671	4057	150.3
Comparative Example 1	-	-	-	-	-	-	3.0	9.2	52	9		404	1680	38.1
Comparative Example 2	-	-	-	-	-	-	1.0	7.2	8	240				

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CLAIMS:

1. Use of a bimodal polypropylene blend in melt processing wherein for enhancing a compromise between melt strength and drawability the blend has a dispersion index M_w/M_n of at least 8, a ratio M_z/M_n of from 50 to 150 and comprises from 50 to 70 wt% of a first high molecular weight fraction and from 50 to 30 wt% of a second low molecular weight fraction.
2. Use according to claim 1 wherein the dispersion index M_w/M_n is greater than 15.
3. Use according to claim 1 or claim 2 wherein the blend comprises from 55 to 65 wt% of the first fraction and from 45 to 35 wt% of the second fraction.
4. Use according to any one of claims 1 to 3 wherein the ratio of the melt flow indexes of the first and second fractions is at least 5, each melt flow index being determined using the procedures of ASTM D1238 using a load of 2.16 kg at a temperature of 230°C.
5. Use according to any foregoing claim wherein the blend has been formed by reactive extrusion of a mixture of at least two fractions together with a mixture of a chain scission agent and a chain grafting agent.
6. Use according to claim 5 wherein the chain scission agent comprises 2,5-dimethyl-2,5-di(tert-butylperoxy) hexane.
7. Use according to claim 5 or claim 6 wherein the chain grafting agent is selected from allyl methacrylate and divinyl benzene.
8. Use according to any foregoing claim for forming spun

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fibres, blown films, foams, thermoformed articles and extrusions.

9. A bimodal polypropylene blend having a dispersion index M_w/M_n of at least 8, a ratio M_z/M_n of from 50 to 150 and comprising from 50 to 70 wt% of a first high molecular weight fraction and from 50 to 30 wt% of a second low molecular weight fraction.

10. A blend according to claim 9 wherein the dispersion index M_w/M_n is greater than 15.

11. A blend according to claim 9 or claim 10 wherein the blend comprises from 55 to 65 wt% of the first fraction and from 45 to 35 wt% of the second fraction.

12. A blend according to any one of claims 9 to 11 wherein the ratio of the melt flow indexes of the first and second fractions is at least 5, each melt flow index being determined using the procedures of ASTM D1238 using a load of 2.16 kg at a temperature of 230°C.

13. A method of melt processing a polypropylene blend, the method comprising providing a bimodal polypropylene blend, selecting the blend to have a dispersion index M_w/M_n of from 8 to 70, a ratio M_z/M_n of from 50 to 150 and from 50 to 70 wt% of a first high molecular weight fraction and from 50 to 30 wt% of a second low molecular weight fraction, and processing the blend in the melt by drawing the blend to form a solid product.

14. A method according to claim 13 wherein the dispersion index M_w/M_n is greater than 15.

15. A method according to claim 13 or claim 14 wherein the blend comprises from 55 to 65 wt% of the first fraction and from 45 to 35 wt% of the second fraction.

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16. A method according to any one of claims 13 to 15 wherein the ratio of the melt flow indexes of the first and second fractions is at least 5, each melt flow index being determined using the procedures of ASTM D1238 using a load of 2.16 kg at a temperature of 230°C.

17. A method according to any one of claims 13 to 16 wherein the blend has been formed by reactive extrusion of a mixture of at least two fractions together with a mixture of a chain scission agent and a chain grafting agent.

18. A method according to claim 17 wherein the chain scission agent comprises 2,5-dimethyl-2,5-di(tert-butylperoxy) hexane.

19. A method according to claim 17 or claim 18 wherein the chain grafting agent is selected from allyl methacrylate and divinyl benzene.

20. A method according to any one of claims 13 to 19 for forming an article selected from spun fibres, blown films, foams, thermoformed articles and extrusions.

Fig. 1

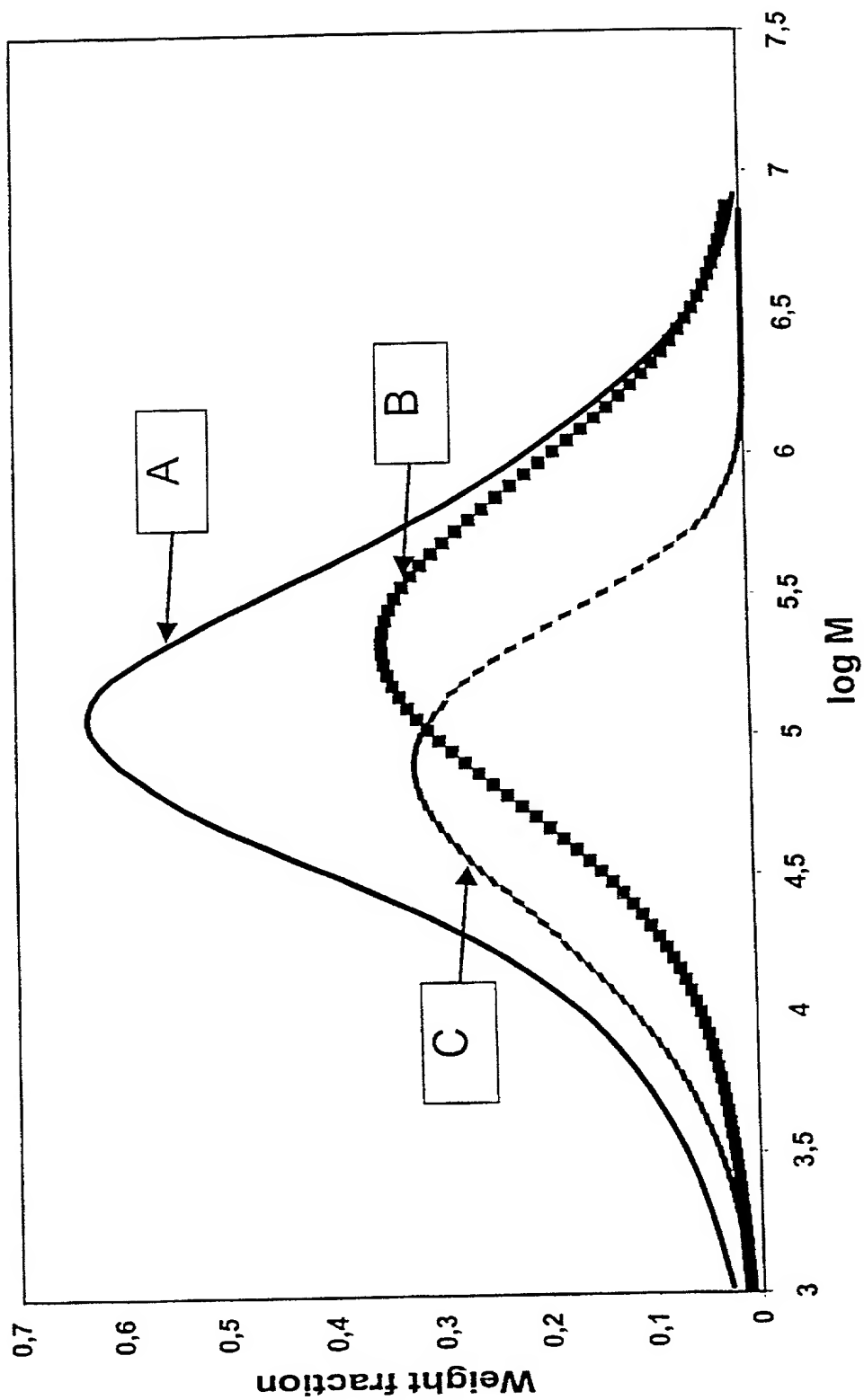


Fig.2

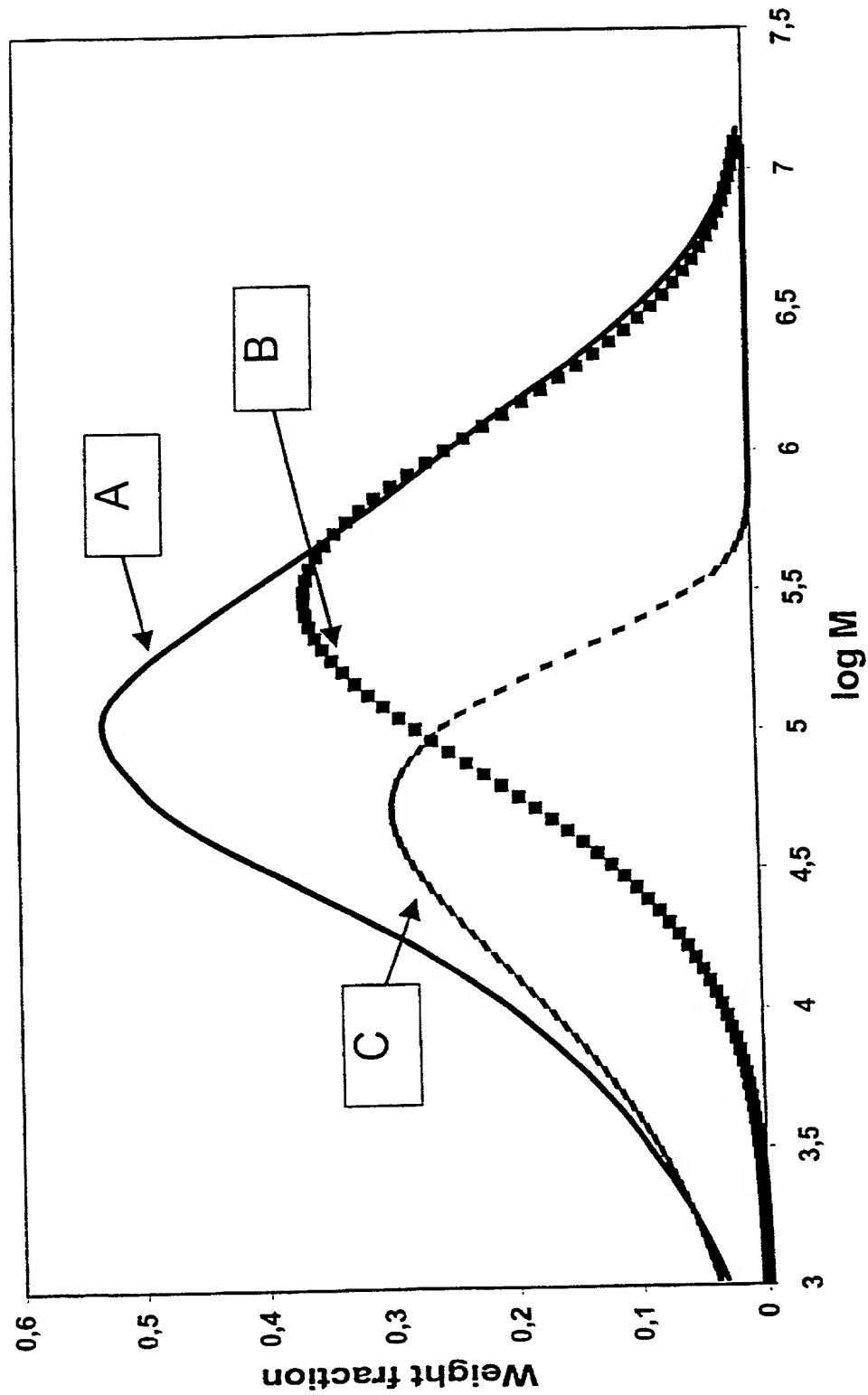
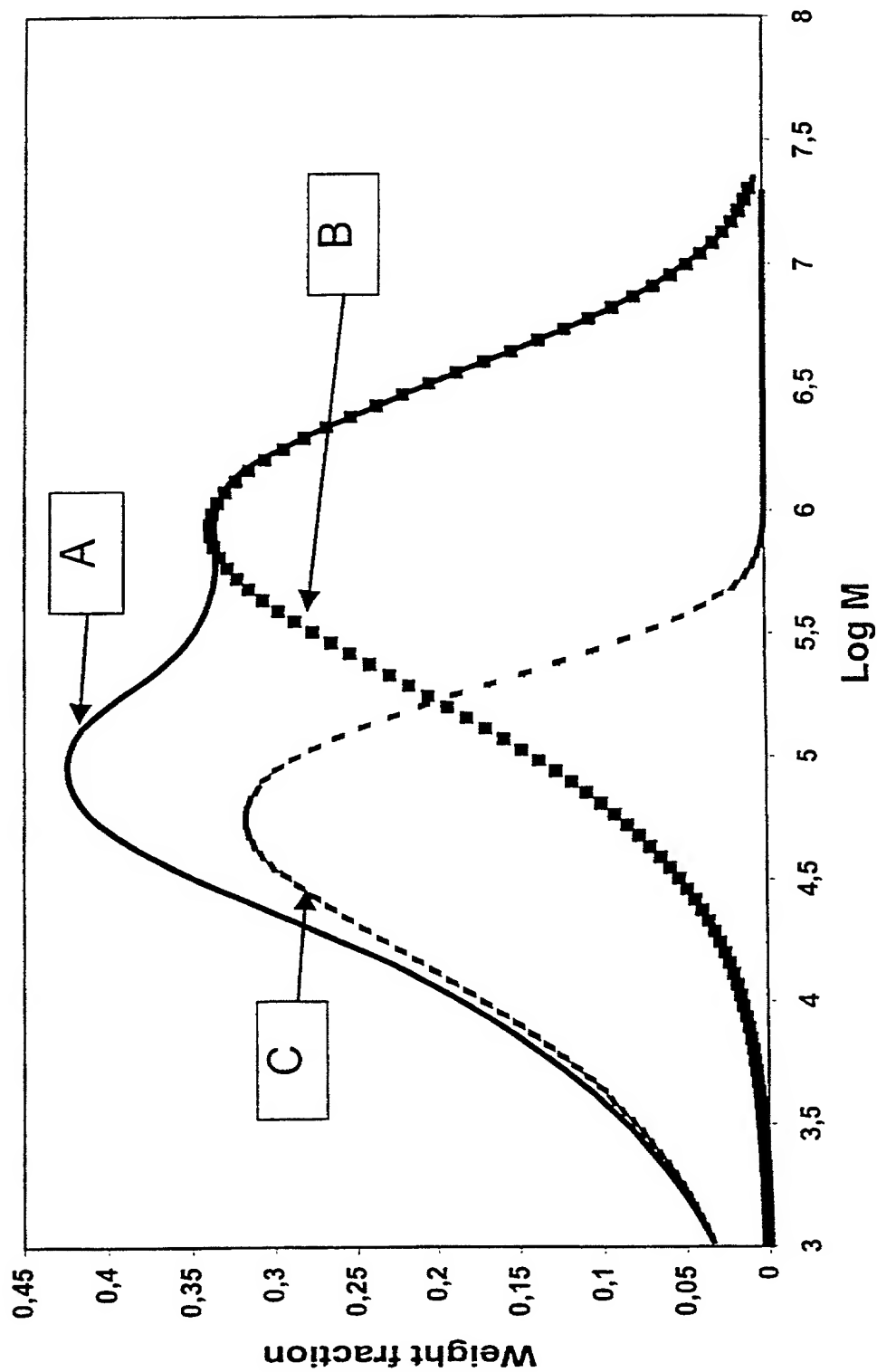


Fig. 3



DECLARATION

As below named inventors, we, MARC DUPIRE and JACQUES MICHEL, hereby declare that:

Our mailing addresses and citizenships are as stated below next to our names.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is described and claimed and for which a patent is sought on the invention, design or discovery entitled: **PROPYLENE WITH HIGH MELT STRENGTH AND DRAWABILITY**, the specification of which was filed December 10, 2001, as Application Serial Number 10/009,625.

We have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

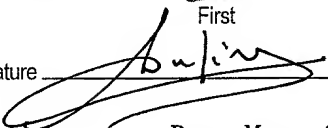
We do not know and do not believe that said invention, design or discovery was ever known or used in the United States of America before our invention or discovery thereof, or patented or described in any printed publication in any country before our invention or discovery thereof, or more than one year prior to this application, or in public use or on sale in the United States of America more than one year prior to this application; that said invention, design or discovery has not been patented or made the subject of an inventor's certificate issued prior to the date of this application in any country foreign to the United States of America on an application filed by our or my legal representatives or assigns.

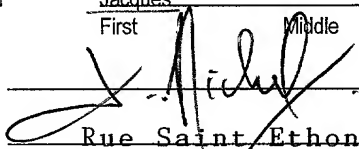
We acknowledge our duty to disclose information of which we are aware which is material to patentability in accordance with 37 C.F.R. Section 1.56(a).

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We hereby declare that all statements made herein of our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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